



Benzocyclobutene-functionalized poly(*m*-phenylene): A novel polymer with low dielectric constant and high thermostability



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ABSTRACT

A novel benzocyclobutene-functionalized poly(*m*-phenylene) was synthesized. This polymer showed good solubility and film-forming ability. When being heated at high temperature, the polymer film converted to an insoluble cross-linked network structure and did not show any cracks. Thermogravimetric analysis of the polymer film exhibited a weight loss of 5% at 547 °C and a char yield of 71% at 1000 °C in nitrogen. Moreover, the cured film had good dielectric and mechanical properties. In a range of frequencies from 0.10 MHz to 30 MHz, the cured film showed dielectric constant of less than 2.7, which was comparable with these of polyimides, polycyanates and the SILK resins. On a nano indenter system, the cured film showed an average hardness of 1.05 GPa and a Yong's modulus of 39.18 GPa. Those data imply that the polymer could be used as the varnish for enameled wire, sizing agents for high performance carbon-fiber, and encapsulation resins in microelectronic industry.

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1. Introduction

Polyphenylenes (PPs) with rigid-rod structure have been well investigated [1–12] and widely used as conductive materials [13,14], optoelectronic materials [1,15–21], chemical sensors for the applications in biology [22], polymeric surfactants [23] and matrix resins in aerospace industry [1c,24]. Recently, PPs with –SO₃H side chains have attracted much attentions because they are of oxidative and water stability and can be used for the fabrication of the proton exchange membranes of fuel cells [25–28].

Of various PPs, poly(*m*-phenylene)s (PMPs) are of particular interest to researchers in the recent years due to their potential applications in the field of chemistry, biology, iatrology and information [29–34]. These polymers consist of meta-linked phenylene units and show a lot of possible conformations including zigzag and helix [32,33]. Such interesting structure not only makes PMPs remain good heat and chemical resistance and good processability but also endows the polymers with the unique properties. For example, Pei and Liu [31] found that PMPs with a carbazole group as the side chain showed very high triplet energy level (E_T), which could be used for fabrication of high performance polymeric electroluminescence diodes. Yashima group [32,33] observed that

PMPs with the short ethyleneoxy chains exhibited a double helix structure in some organic solvents, and such type of PMPs may have potential application in biology. Therefore, PMPs have been considered as promising candidates for high-performance materials [29].

However, in many cases, the obtained PMPs showed low molecular weight [35], which may cumber the application of PMPs. To improve this situation, A. D. Schlüter and coworkers [34] adopted copolymerization of *p*-phenylene and *m*-phenylene monomers under Suzuki coupling condition. The obtained copolymers showed good mechanical properties and was expected to be used as high performance materials. More recently, J. Sakamoto group [29] employed Suzuki coupling from an AB monomer containing both boric ester and bromo group to give high molecular weight of PMPs, whereas the polymerization gave a mixture of cyclic oligomers and open-chain products. Accordingly, further investigation on the synthesis and properties of PMPs is still necessary.

To our knowledge, for the polymers that were obtained by a step-growth polymerization procedure, like the synthesis of PMPs, an efficient and simple strategy to enhance their molecular weight is to introduce the addition-type reactive groups into the side chains or the backbone of the polymers. Such reactive groups can form chain-extended products via an addition-polymerization process [24]. It is known that benzocyclobutene (BCB) is a molecule with high reactivity [36], and BCB-functionalized oligomers or polymers have been recognized as a new generation of high

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performance materials for microelectronic applications [37–39]. At high temperature, the four-membered-ring on **BCB** opens to produce a highly reactive *o*-quinodimethane intermediate [36], which can react with itself to form a dimer, or attacks available dienophiles to give a Diels–Alder adduct [35]. Importantly, the *o*-quinodimethane intermediate usually has a tendency to polymerize to form poly(*o*-xylylene) [36]. The characteristic of **BCB** inspires us to develop new **PMPs**. Our strategy is introducing **BCB** moieties into the backbone of **PMPs** to produce functional **PMPs**, which can be readily converted to crosslinking matrixes at heating. Thus, the obtained functional **PMPs** would exhibit good processability and high heat resistance, and they could be used as the varnish for enameled wire, sizing agents for high performance carbon-fiber, and encapsulation resins of integrated circuit (IC) dies. This is the first example of **PMPs** containing thermocrosslinkable groups. Herein, we report the details.

2. Experimental

2.1. Materials

The starting chemicals were purchased from Aldrich and used as received unless otherwise stated. Benzocyclobutene-4-boronic acid was purchased from Chemtarget Technologies Co., Ltd., China, and purified by chromatograph on SiO₂ using a mixture of ethyl acetate and *n*-hexane (40:1, v/v) as the eluent.

2.2. Measurements

¹H NMR and ¹³C NMR spectra were carried out on a Bruker 400 spectrometer. FT-IR spectra were recorded on a Nicolet spectrometer with KBr pellets. Differential scanning calorimetry (DSC) was determined with TA Instrument DSC Q200 at a heating rate of 10 °C min⁻¹ under nitrogen flow. Thermogravimetric analysis (TGA) was performed on a TG 209F1 apparatus with a heating rate of 10 °C min⁻¹ in a nitrogen atmosphere. The dielectric constant (*k*) and the dielectric loss (tan δ) of the cured samples were measured in the range of frequency from 0.1 MHz to 30 MHz at room temperature using a 4294A Precision Impedance Analyzer (Agilent). The contact angles of the cured samples were measured at 20 ± 1 °C using a sessile drop method on a dynamic contact angle measurement instrument (JC2000C). Deionized water was selected as the testing liquid.

2.3. Synthesis of monomer **1**

To a stirring solution of 1-bromo-3,5-dichlorobenzene (27.12 g, 120 mmol), benzocyclobutene-4-boronic acid (5.84 g, 40 mmol), tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄) (2.312 g, 2 mmol) and toluene (200 mL) was added aq Na₂CO₃ (21.2 g, 200 mmol, in 50 mL water) under argon. The mixture was heated to 90 °C and the temperature was remained for 12 h. After being cooled to room temperature, the reaction mixture was filtered to remove the solid, and the filtrate solution was concentrated. The obtained residue was purified by flash chromatography on silica gel using hexane as an eluent to afford **1** as a white solid (5.98 g, yield of 60%). Characterization: ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.42 (d, *J* = 1.6 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 1.6 Hz, 1H), 7.22 (s, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 3.24 (s, 4H), ¹³C NMR (100 MHz, CDCl₃, ppm): δ 146.55, 146.29, 145.32, 137.54, 135.08, 126.65, 126.03, 125.70, 123.01, 121.37, 29.51, 29.48, HRMS Calcd for C₁₄H₁₀C₁₂ [M]⁺: 248.0160, found: 248.0165, Anal. Calcd for C₁₄H₁₀C₁₂: C, 67.49, H, 4.05, Cl, 28.46, found: C, 67.74, H, 4.16, Cl, 28.48.

2.4. Synthesis of the polymer (**PMP–BCB**)

To a 20 mL of Schlenk tube charged with NiBr₂ (22 mg, 0.1 mmol), PPh₃ (131 mg, 0.5 mmol), 2,2'-bipyridine (BPY, 16 mg, 0.1 mmol) and zinc dust (1.625 g, 5 mmol) was added dry DMAC (5 mL) under argon. The mixture was stirred for 1 h. When the solution changed to red brown, **1** (1.245 g, 5 mmol) was added. The temperature was allowed to increase to 80 °C, and the mixture was stirred at the temperature for 36 h. The resulting black mixture was diluted with 50 mL of DMAC, filtered through celite, and then poured into 200 mL of methanol containing concentrated HCl (2 mL). The polymer precipitate was collected by filtration, washed with methanol, and dried in a vacuum at 100 °C for 24 h. Characterization: ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.03 (m, 1H), 7.94 (m, 2H), 7.60 (m, 1H), 7.46 (m, 1H), 7.16 (m, 1H), 3.27–3.25 (m, 4H), ¹³C NMR (100 MHz, CDCl₃, ppm) δ 146.41, 145.36, 143.80, 142.45, 140.07, 126.44, 125.87, 125.21, 122.91, 121.84, 29.54, 29.48. Anal. Calcd for (C₁₄H₁₀)_n: C, 94.34, H, 5.66, found: C, 93.90, H, 5.76.

2.5. Curing of the polymer

A solution of the obtained polymer (**PMP–BCB**) in trimethylbenzene was spin-coated on the surface of a glass sheet. After the solvent was removed at 110 °C under reduced pressure, a transparent film was obtained. This film became pale-yellow in color after being heated at 250 °C for 5 h under N₂ and was no longer soluble in organic solvents.

To prepare the cured **PMP–BCB** film used for the measurement of dielectric constant, the procedure was as following: on an aluminum-backed silicon wafer (heavily doped single crystal silicon with a resistivity of 0.0035 Ω-cm), a solution of **PMP–BCB** in trimethylbenzene was spin-coated to form a film. The wafer was heated at 250 °C for 5 h under N₂ in a quartz tube furnace. Finally, aluminum was deposited via vacuum evaporation on the surface of the film as a top electrode (the diameter = 4.2 mm). The thickness of cured **PMP–BCB** was measured by scanning electron microscopy (SEM).

3. Results and discussion

3.1. Synthesis and characterization and solubility of the benzocyclobutene-functionalized poly(*m*-phenylene)

The procedure for the synthesis of the monomer **1** and polymer **PMP–BCB** is depicted in Scheme 1. As shown in Scheme 1, monomer **1**, **BCB**-substituted dichlorobenzene, was prepared in a yield of 60% using the standard Suzuki coupling reaction between bromodichlorobenzene and benzocyclobutene-4-boronic acid. The polymerization was carried out under Ullmann coupling condition [12,35] in the presence of a catalyzed system, comprising of NiBr₂, triphenylphosphine (PPh₃), 2,2'-bipyridine (BPY) and zinc dust. Analysis by GPC (polystyrene standards) showed that the polymer had *M_n* (number average molecular weight) and PDI (polydispersion index) values of 7800 and 1.15, respectively. According to the *M_n*, the number of the repeating unit of the polymer is estimated at about 44, which was much higher than that of previously reported **PMPs**, prepared by the Ullmann coupling reaction [35].

The chemical structures of the obtained polymer, **PMP–BCB**, were characterized by its ¹H {¹³C} NMR spectra and elemental analysis. Fig. 1 gives ¹H NMR spectrum of **PMP–BCB**. As can be seen from Fig. 1, all data are consistent with the proposed. For example, the peaks at 8.03–7.16 ppm are attributed to the protons at the aromatic rings, and the peak at 3.26 ppm is derived from the H at

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